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(54) PRODUCTION OF MICROCRUYSTALLINE PERMANENT MAGNET ALLOY AND PERMANENT MAGNET POWDER

(57)Abstract:
PROBLEM TO BE SOLVED: To moderate manufacturing conditions, particularly heat treatment conditions, and to perform stable industrial production by subjecting a molten alloy, which has a composition prepared by regulating the concentration of rate earths in an Nd-Fe-B alloy to a specific value or bellow and a specific amount of B is contained, to allowing in an inert gas atmosphere with an atmospheric pressure in a specific range by means of liquisol quenching using a cooling roll.
SOLUTION: A molten alloy, represented by a composition formula $Fe_{100-x-y}B_xR_y$ (where R is one or more elements among Pr, Nd, Dy, and Tb) in which (x) and (y) satisfy $15 \leq x \leq 30$ atomic % and $1 \leq y \leq 6$ atomic %, respectively, is continuously cast on a rotating cooling roll in an inert gas atmosphere of 31 to 101 kPa. By this procedure, a microcrystalline alloy, having a structure in which a crystalline structure, where an Fe_3B type compound phase of ≤10 nm average crystalline grain size, an α-Fe phase, and a compound phase with $Nb_2Fe_{14}B$ type crystalline structure coexist, comprises ≥50% and the balance is compound of amorphous structure, is prepared. This alloy is heat-treated at 550 to 750° C and formed into a microcrystalline alloy of 10 to 50 nm average crystalline grain size, and the magnetic alloy having magnetic properties of iHc≥2 kOe and Br≥8 kG can be obtained.

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CLAIMS

[Claim(s)]

[Claim 1] an empirical formula -- Fe100-x-yBxRy (however, R -- one sort of Pr, Nd, Dy, or Tb, or two sorts or more) It expresses. ** -- The notation x which limits the presentation range, and the molten metal with which y is satisfied of the following value in the inert gas ambient atmosphere of 31kPa-101kPa Cast continuously on the rotating cooling roller and the crystalline structure where the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm or less of diameters of average crystal grain lives together occupies 50% or more. By producing the fine crystal alloy with which the remainder consists of an amorphous substance, and heat-treating after that in a 550 degrees C - 750 degrees C temperature region The manufacture approach of a fine crystal permanent magnet alloy of obtaining the fine crystal alloy of 10nm - 50nm of diameters of average crystal grain, and the magnet alloy which has the magnetic properties of nothing, iHc>=2kOe, and Br>=8kG.

15 <=x <=30at% -- 1 <=y<6at% -- [Claim 2] an empirical formula -- 100(Fe1-mCom)-x-yBxRy (however, R -- Pr --) The notation x which expresses one sort of Nd, Dy, or Tb, or two sorts or more, and limits the presentation range, The molten metal with which y and m are satisfied of the following value in the inert gas ambient atmosphere of 31kPa-101kPa Cast continuously on the rotating cooling roller and the crystalline structure where the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm or less of diameters of average crystal grain lives together occupies 50% or more. By producing the fine crystal alloy with which the remainder consists of an amorphous substance, and heat-treating after that in a 550 degrees C - 750 degrees C temperature region The manufacture approach of a fine crystal permanent magnet alloy of obtaining the fine crystal alloy of 10nm - 50nm of diameters of average crystal grain, and the magnet alloy which has the magnetic properties of nothing, iHc>=2kOe, and Br>=8kG.

15 <=x <=30at%1<=y -- < -- 6at%0.001 <=m<=0.5 -- [Claim 3] an empirical formula -- Fe100-x-y-zBxRyMz (however, R -- Pr --) One sort of Nd, Dy, or Tb or two sorts or more, and M aluminum, Si, Ti, V, Cr, Mn, nickel, Cu, Ga, Zr, Nb, Mo, Ag, Pt, The notation x which expresses one sort of Au and Pb, or two sorts or more, and limits the presentation range, The molten metal with which y and z are satisfied of the following value in the inert gas ambient atmosphere of 31kPa-101kPa Cast continuously on the rotating cooling roller and the crystalline structure where the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm or less of diameters of average crystal grain lives together occupies 50% or more. By producing the fine crystal alloy with which the

remainder consists of an amorphous substance, and heat-treating after that in a 550 degrees C - 750 degrees C temperature region The manufacture approach of a fine crystal permanent magnet alloy of obtaining the fine crystal alloy of 10nm - 50nm of diameters of average crystal grain, and the magnet alloy which has the magnetic properties of nothing, iHc>=2kOe, and Br>=8kG.

15 <=x <=30at%1 <=y<6at%0.01 <=z<=7at% -- [Claim 4] an empirical formula -- 100(Fe1-mCom)-x-y-zBxRyMz (however, R -- Pr --) One sort of Nd, Dy, or Tb or two sorts or more, and M aluminum, Si, Ti, V, Cr, Mn, nickel, Cu, Ga, Zr, Nb, Mo, Ag, Pt, The notation x which expresses one sort of Au and Pb, or two sorts or more, and limits the presentation range, The molten metal with which y, z, and m are satisfied of the following value in the inert gas ambient atmosphere of 31kPa-101kPa Cast continuously on the rotating cooling roller and the crystalline structure where the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm or less of diameters of average crystal grain lives together occupies 50% or more. By producing the fine crystal alloy with which the remainder consists of an amorphous substance, and heat-treating after that in a 550 degrees C - 750 degrees C temperature region The manufacture approach of a fine crystal permanent magnet alloy of obtaining the fine crystal alloy of 10nm - 50nm of diameters of average crystal grain, and the magnet alloy which has the magnetic properties of nothing, iHc>=2kOe, and Br>=8kG.

15 <=x <=30at%1<=y -- < -- 6at%0.01 <=z<=7at%0.001 <=m<=0.5 -- [Claim 5] The manufacture approach of isotropic permanent magnet powder of having the fine crystal organization which gets the magnet powder which grinds the obtained fine crystal permanent magnet alloy in claim 1, claim 2, claim 3, or claim 4 in average powder particle size of 3 micrometers - 500 micrometers, and has the magnetic properties of iHc>=2kOe and Br>=7kG.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the optimal permanent magnet alloy for the magnetic circuit for various small motors, an actuator, and magnetic sensors etc., and permanent magnet powder. By casting the alloy molten metal of a specific presentation continuously on the cooling roller which rotates the molten metal of the specific presentation containing the rare earth elements not more than 6at%, and 15at(s)% - 30at% boron among a specific reduced pressure inert gas ambient atmosphere The crystalline structure where the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm or less of diameters of average crystal grain lives together occupies 50% or more. By producing the fine crystal alloy with which the remainder consists of an amorphous substance, and heat-treating after that in a 550 degrees C - 750 degrees C temperature region By grinding the permanent magnet alloy which has the magnetic properties of iHc>=2kOe and Br>=8kG by carrying out grain growth of the diameter of average crystal grain to 10nm - 50nm, or a permanent magnet alloy It is related with the manufacture approach of the fine crystal permanent magnet alloy which can obtain iHc>=2kOe which is equal to practical use as magnet powder for bond magnets, and the permanent magnet powder which has the magnetic properties of Br>=7kG, and permanent magnet powder.

[0002]

[Description of the Prior Art] In current, the device for household electric appliances, OA equipment, electronic autoparts, etc., much more high-performance-izing and small lightweight-ization are demanded, and as the whole magnetic circuit using a permanent magnet Although the design for making an engine-performance tare quantitative ratio into max is considered and the residual magnetic flux density Br is made the optimal [what is 5kG(s) - 7kG extent] as a permanent magnet with the structure of the DC motor with a brush which has the great portion of present number of production especially It cannot obtain with the conventional hard ferrite magnet.

[0003] For example, although it is satisfied with the Nd-Fe-B sintered magnet and Nd-Fe-B bond magnet which make Nd2Fe14B the main phase of these magnetic properties Nd which a process list great for metaled separation purification and a metaled reduction reaction takes a large-scale facility -- 10at(s)% - 15at%, since it contains As compared with a hard ferrite magnet, it becomes it is remarkable and expensive, and the alternative from a hard ferrite magnet progresses only from some models in respect of a price performance, now, it has Br of 5 or more kGs, and the cheap permanent magnet ingredient is not

found out.
[0004]
[Problem(s) to be Solved by the Invention] On the other hand, in the Nd-Fe-B system magnet, the magnet ingredient which carries out the main phase of the Fe3B mold compound by presentation near Nd4Fe77B19 (at%) is proposed (R. J.de Phys(es), such as Coehoorn, C8, 1988, 669-670 page), and the technical contents are indicated by U.S. Pat. No. 4,935,074 etc. in recent years.
[0005] Moreover, Koon has proposed the manufacture approach of the permanent magnet which consists of a fine crystal by performing heat-of-crystallization processing to the La-R-B-Fe amorphous alloy which contains La as an essential element before in U.S. Pat. No. 4,402,770 rather than it.
[0006] recently, it is indicated by Richter and others at EP JP,558691,B B1 -- as -- Nd :- 3.8at(s)% - 3.9at% -- by heat-treating the amorphous flake injected and obtained on Cu roll turning around the Nd-Fe-B-V-Si alloy molten metal to contain at 700 degrees C has reported that a flake with hard magnetic property is obtained.
[0007] These permanent magnet ingredients are permanent magnet ingredients of the metastable structure of having the crystal texture where Fe3 B phase which is the soft magnetism and the R2Fe14 B phase which is the hard magnetism obtained by performing heat-of-crystallization processing to an amorphous flake with a thickness of 20 micrometers - 60 micrometers are intermingled.
[0008] Although this permanent magnet ingredient has Br of 10kG extent, and iHc of 2kOe-3kOe, and a feed ingredient price is cheaper than the Nd-Fe-B magnet which makes Nd2Fe14B the main phase since the expensive content concentration of Nd is as low as about 4at% The heat treatment conditions for liquid quenching conditions being limited since it is necessary to carry out 90% or more amorphous substance alloying of the feed ingredient of real, and becoming a hard magnetic material to coincidence are limited narrowly, and it is not practical on industrial production and cannot provide cheaply as an alternative of a hard ferrite magnet.
[0009] On the other hand, although the organization which consists of a crystalline substance which has direct and hard magnetic property by quenching an alloy molten metal with roll peripheral-velocity 20 m/s extent can be obtained with super-quenching Nd-Fe-B system magnet ingredients, such as U.S. Pat. No. 508,266, since expensive Nd content contained into an alloy is as high as about 13at%, it cannot provide cheaply as an alternative of a hard ferrite magnet.
[0010] In the permanent magnet ingredient of the metastable structure where, as for this invention, rare earth concentration has the crystal texture where Fe3 B phase of soft magnetism and the Nd2Fe14 B phase of hard magnetism which are characterized by less than [6at%] and the low thing are intermingled It aims at making possible industrial production which eased the manufacture condition, especially heat treatment conditions, and was stabilized. It aims at offer of the manufacture approach of the fine crystal permanent magnet alloy which enables mass production of the fine crystal permanent magnet alloy which has especially the residual magnetic flux density Br of 8 or more kGs, and has the price performance which is equal to a hard ferrite magnet.
[0011]
[Means for Solving the Problem] The result to which artificers considered various the manufacture approaches of the Nd-Fe-B system fine crystal permanent magnet of low rare earth concentration that a soft magnetism phase and a hard magnetism phase were intermingled, The alloy molten metal of the specific presentation in which there are few contents of rare earth elements as less than [6at%], and they

contain 15at% - 30at% B By facing carrying out quenching alloying with the melt quenching method using a cooling roller, and quenching in the inert gas ambient atmosphere of 31kPa-101kPa The liquid quenching conditions which needed to be made amorphous in 90% or more of parenchyma are eased conventionally. While the deposit of alpha-Fe of 100nm or more of crystal grain parameters which carry out the cause of the degradation of magnetic properties is controlled also on the liquid quenching conditions that the crystalline structure of a quenching alloy occupies 50% or more Then, in case it heat-treats in a 550 degrees C - 750 degrees C temperature region, the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm - 50nm of diameters of average crystal grain lives together. The knowledge of the heat-treatment-temperature range which can obtain the fine crystal permanent magnet alloy which obtains the magnet alloy which has the magnetic properties of iHc>=2kOe and Br>=8kG being expanded was carried out, and this invention was completed.

[0012] This invention an empirical formula Namely, Fe100-x-yBxRy, 100(Fe1-mCom)-x-yBxRy, Fe100-x-y-zBxRyMz and 100(Fe1-mCom)-x-y-zBxRyMz (however, R -- Pr --) One sort of Nd, Dy, or Tb or two sorts or more, and M aluminum, Si, Ti, V, Cr, Mn, nickel, Cu, Ga, Zr, Nb, Mo, Ag, Pt, The notation x which expresses with either one sort or two sorts or more, Au and Pb, and limits the presentation range, The molten metal with which y, z, and m are satisfied of the following value in the inert gas ambient atmosphere of 31kPa-101kPa Cast continuously on the rotating cooling roller and the crystalline structure where the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm or less of diameters of average crystal grain lives together occupies 50% or more. By producing the fine crystal alloy with which the remainder consists of an amorphous substance, and heat-treating after that in a 550 degrees C - 750 degrees C temperature region The manufacture approach of a fine crystal permanent magnet alloy of obtaining the fine crystal alloy of 10nm - 50nm of diameters of average crystal grain and the magnet alloy which has the magnetic properties of nothing, iHc>=2kOe, and Br>=8kG is proposed.

15 <=x <=30at%1 <=y<6at%0.01 <=z<=7at%0.001 <=m<=0.5[0013] Furthermore, this invention grinds the fine crystal permanent magnet alloy obtained by the above-mentioned manufacture approach in average powder particle size of 3 micrometers - 500 micrometers, and proposes collectively the manufacture approach of isotropic permanent magnet powder of having the fine crystal organization which gets the magnet powder which has the magnetic properties of iHc>=2kOe and Br>=7kG.

[0014]

[Embodiment of the Invention]

The reason rare earth elements R for limitation of a presentation are not desirable, in order that one sort or the magnetic properties high only at the time of the amount content of specification two or more sorts of Pr, Nd, Dy, or Tb may be acquired, and the property of 2 or more kOes may not be acquired for iHc with other rare earth, for example, Ce and La, and the inside rare earth elements after Sm except Tb and Dy and a heavy-rare-earth element may invite degradation of magnetic properties. Less than [1at%], since iHc of 2 or more kOes is not obtained, and Br of 8 or more kGs will not be obtained if 6at(s)% is exceeded, R is taken as the range below more than 1at%6at%. It is good 2at% - 5.5at% of preferably.

[0015] Less than [15at%], in the metal texture after liquid quenching, the deposit of alpha-Fe of B is remarkable, and since only iHc of less than 1 kOe is obtained since the deposit of a compound which has the indispensable Nd2Fe14B mold crystal structure in the manifestation of coercive force is checked, and

the square shape nature of a demagnetization curve will fall remarkably and Br of 8 or more kGs will not be obtained if 30at(s)% is exceeded, it is taken as the range of 15at% - 30at%. It is good 15at% - 20at% of preferably.

[0016] Although Fe occupies the content remainder of an above-mentioned element, a metal texture is made detailed by permuting a part of Fe by Co and the improvement in thermal resistance [nature / of a demagnetization curve / square shape] is obtained by an improvement and improvement in maximum energy product (BH) max, and the list Since Br of 8 or more kGs will not be obtained if this effectiveness is not acquired at less than 0.1% and the amount of permutations to Fe exceeds 50%, let the amount of permutations to Fe of Co be 0.1% - 50% of range. It is good 0.5% - 10% of preferably.

[0017] aluminum, Si, Ti, V, Cr, Mn, nickel, Cu, Ga, Zr, Nb, Mo, Ag, Pt, Au, and Pb of an alloying element M Although the effectiveness which improves the square shape nature of a demagnetization curve and increases Br and (BH) max is acquired while contributing to detailed systematization of a fine crystal permanent magnet and improving coercive force This effectiveness is not acquired, but more than at 7at%, since the magnetic properties of Br>=8kG cannot be acquired, it considers as the range of 0.01at% - 7at% less than [0.01at%]. Preferably, it is 0.05at% - 5at%.

[0018] In invention of limited ****** of manufacture conditions the alloy molten metal of an above-mentioned specific presentation in the inert gas ambient atmosphere of the range of 31kPa-101kPa Cast continuously on the rotating cooling roller and the crystalline structure where the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm or less of diameters of average crystal grain lives together occupies 50% or more. By producing the fine crystal alloy with which the remainder consists of an amorphous substance, and heat-treating after that in a 550 degrees C - 750 degrees C temperature region It is most important to make with the fine crystal organization of 10nm - 50nm of diameters of average crystal grain required to obtain the magnet alloy which has the magnetic properties of iHc>=2kOe and Br>=8kG.

[0019] Namely, when a casting ambient atmosphere exceeds 101kPa(s) in the case of the continuous casting of an alloy molten metal By turbulence of the molten metal style by the gas contamination between a roll and a molten metal, and the wind of the roll circumference etc. Become a quenching alloy organization containing big and rough alpha-Fe which is 100nm of crystal grain parameters by which cooling conditions are not stabilized, and the magnetic properties of iHc>=2kOe and Br>=8kG are not acquired, but when it is less than 31 kPas Since the amorphous organization potency which changes depending on an alloy presentation increases, it is easy to become fault quenching and the magnetic properties after heat treatment are not stabilized, a molten metal quenching ambient atmosphere is set to 31kPa-101kPa. Preferably, 31kPa-80kPa is good. A controlled atmosphere is made into an inert gas ambient atmosphere for antioxidizing of an alloy molten metal. Preferably, the inside of N2 and Ar ambient atmosphere is good.

[0020] Although it is necessary to perform heat treatment aiming at grain growth so that the above-mentioned quenching alloy may become the metal texture which consists of a fine crystal of 10nm - 50nm of diameters of average crystal grain required to obtain the permanent magnet alloy which has the magnetic properties of iHc>=2kOe and Br>=8kG In order that heat treatment temperature may not cause grain growth at less than 550 degrees C, the diameter of average crystal grain 10nm or more is not obtained. Moreover, since the grain growth exceeding 750 degrees C is remarkable, iHc, Br, and the square shape nature of a demagnetization curve deteriorate and above-mentioned magnetic properties

are not acquired, heat treatment temperature is limited to 550 degrees C - 750 degrees C.

[0021] In heat treatment, the inside of inert gas ambient atmospheres, such as Ar gas and N2 gas, or a vacuum 1.33Pa or less of an ambient atmosphere is desirable in order to prevent oxidation. Although it is not dependent on heat treatment time amount, since magnetic properties have the inclination for Br to fall with the passage of time a little when exceeding 6 hours, its less than 6 hours are preferably good.

[0022] Although an aluminium alloy, a pure copper and a copper alloy, iron, brass, a tungsten, and bronze can be used for the quality of the material of the cooling roller used for liquid quenching continuous casting processing of an alloy molten metal from the point of thermal conductivity Since the point of a mechanical strength and economical efficiency to Cu or Fe (however, the alloy containing Cu and Fe is sufficient) is desirable and heat conduction is bad with the quality of the materials other than the above, Since an alloy molten metal cannot be cooled enough but several 100nm big and rough alpha-Fe and Fe2B deposit, the magnetic properties of iHc>=2kOe and Br>=8kG cannot be acquired, and it is not desirable.

[0023] To a cooling roller, for example, center line granularity Ra<=0.8micrometer, maximum height Rmax<=3.2micrometer, When the roll made from Cu which has the average-of-roughness-height Rz<=3.2micrometer surface roughness of ten points is adopted, The crystalline structure included in a quenching alloy when roll peripheral velocity exceeds 15 m/s becomes 50% or less. The metal texture of a quenching alloy becomes uneven, the magnetic properties after heat treatment are not stabilized, but since it is not desirable, roll peripheral velocity has 4 m/s - 15 m/s good [since an amorphous phase increases, it is not desirable and] when roll peripheral velocity is 4 or less m/s.

[0024] Moreover, the end of isotropic permanent magnet magnetic powder it has iHc>=4kOe and Br>=7kG can be obtained by grinding the fine crystal permanent magnet alloy by this invention so that it may become the grain size of 3 micrometers - 500 micrometers. If powder particle size falls [magnetic properties, especially Br] in less than 3 micrometers and is not desirable and 500 micrometers is exceeded, since shaping is difficult, the magnetic powder grain size after grinding will be limited to 3 micrometers - 500 micrometers. When using as magnetic powder for compression-molding bond magnets, 10 micrometers - 300 micrometers are desirable, and as magnetic powder for injection-molding bond magnets, 50 micrometers or less are desirable.

[0025] The Fe3B mold compound and alpha-Fe which have soft magnetism, and the hard magnetism compound phase which has the Nd2Fe14B mold crystal structure live together during the same organization, and the crystal phase of the fine crystal permanent magnet alloy by this invention is characterized by consisting of the fine crystal aggregate of the range whose diameter of average crystal grain of each configuration phase is 10nm - 50nm. If the diameter of average crystal grain which constitutes a fine crystal permanent magnet alloy exceeds 50nm, Br and the square shape nature of a demagnetization curve deteriorate, and the magnetic properties of Br>=8kG cannot be acquired. Moreover, by less than 10nm, although the diameter of average crystal grain is so desirable that it is fine, in order to cause the fall of iHc, a minimum is set to 10nm.

[0026]

[Example]

So that it may become the presentation of example 1 table 1 of No.1-17 Fe of 99.5% or more of purity, Co, aluminum, Si, Ti, V, Cr, Mn, nickel, Cu, Ga, Zr, The metal of Nb, Mo, Ag, Pt, Au, Pb, B, Nd, Pr, Dy, and Tb is used. Carry out weighing capacity so that a total amount may be set to 30g, and it supplies in the quartz crucible which has an orifice with a diameter of 0.8mm at the pars basilaris ossis occipitalis. It

dissolves by high-frequency heating in Ar ambient atmosphere held to the quenching ambient pressure of Table 1. After making a melting temperature into 1300 degrees C, the surface of hot water is pressurized by Ar gas. At a room temperature The molten metal was cast from height of 0.7mm in succession to the peripheral face of the cooling roller made from Cu which rotates with the quenching ambient atmosphere and roll peripheral velocity which are shown in Table 1, and the quenching alloy of the continuous shape of sheet metal with a width of face [of 2mm - 3mm] and a thickness of 100 micrometers - 300 micrometers was produced.

[0027] This quenching alloy was held for 10 minutes with the heat treatment temperature shown in Table 1 in Ar gas, was cooled to the room temperature after that, the alloy was taken out, the sample with width of face of 2-3mm, a thickness [of 50 micrometers - 200 micrometers], and a die length of 3-5mm was produced, and it measured in VSM. A magnet property is shown in Table 2. In No.3-No.17, Co, aluminum, Si, Ti, V, Cr, Mn, nickel, Cu, Ga, Zr, Nb, Mo, Ag, Pt, Au, and Pb permute a part of Fe of each configuration phase.

[0028] As the coercive force dependency over the heat treatment temperature in example No.8 of drawing 1 shows, it depends on heat treatment temperature for the coercive force of the quenching alloy obtained by this invention. In the quenching alloy of example No.1-No.17, the heat-treatment-temperature region where iHc of 2 or more kOes is obtained is shown in Table 3.

[0029] About No.6 of example 2 table 1, No.7, No.8, and the quenching alloy of No.13, it ground so that it might become the grinding grain size of 25 micrometers - 300 micrometers, and the average powder particle size of 150 micrometers using a grinder, and isotropic permanent magnet powder was produced. The magnetic properties of the magnet powder measured in VSM are shown in Table 4.

[0030] The quenching alloy was produced on the quenching conditions shown in Table 1 using Fe, B, R, and Si of 99.5% of purity so that it may become the presentation of example of comparison 1 table 1 of No.18-No.21. It heat-treated into the obtained quenching alloy, and after cooling, the sample was produced on the same conditions as an example 1, and magnetic properties were evaluated using VSM. An evaluation result is shown in Table 2.

[0031] Although it is dependent on heat treatment temperature as the coercive force dependency over the heat treatment temperature of drawing 1 shows the magnetic properties of example No.of comparison 19, the heat-treatment-temperature region which coercive force discovers is narrow compared with example No.8 obtained in quenching ambient pressure 60kPa. In the quenching alloy of example No.of comparison18-No.21, the heat-treatment-temperature region where iHc of 2 or more kOes is obtained is shown in Table 3.

[0032]

[Table 1]

		組成(at%)				ロール周速度	急冷雰囲気圧	熱処理温度
		Fe	B	R	M	m/秒	kPa	℃
実施例	1	79.5	18.5	Nd2	-	10	50	590
	2	78.5	18.5	Nd3	-	15	80	620
	3	75+Co3	17.5	Nd3.5+Pr1	-	7	50	640
	4	70+Co2	20	Nd5	V3	7	40	660
	5	77+Co3	15.5	Nd4	Zr0.5	4	40	640
	6	66+Co5	18.5	Nd5.5	Cr5	12	31	700
	7	78	17	Nd3	Al2	8	70	600
	8	76.5	18.5	Nd4	Si1	5	60	680
	9	69	18.5	Nd3.5+Dy1	Mn1	10	80	640
	10	76	20	Nd5	Ni1.5	10	50	660
	11	75	20	Nd2.5+Pr1	Cu1.5	10	50	610
	12	77	18.5	Nd2+Dy2	Nb0.5	10	50	620
	13	75.5	18.5	Nd2+Pr3	Ga1	8	40	660
	14	76.5	18.5	Nd4	Ag1	8	40	660
	15	78	18	Nd3.5	Pt0.5	8	40	600
	16	76.5	18.5	Nd4.5	Au0.5	6	55	640
	17	75.5	18.5	Nd4.5+Tb0.5	Pb1	9	35	680
比較例	18	78.5	18.5	Nd3	-	30	110	615
	19	76.5	18.5	Nd4	Si1	20	110	660
	20	75.5	18.5	Nd3	-	10	110	620
	21	76.5	18.5	Nd4	Si1	5	110	670

[0033]

[Table 2]

		磁石特性		
		Br (kG)	iHc (kOe)	(BH)max (MGOe)
本発明	1	15.0	2.0	13.5
	2	13.7	2.7	15.0
	3	11.4	4.2	14.7
	4	10.0	6.0	12.2
	5	12.3	4.5	15.5
	6	10.1	6.9	12.9
	7	13.4	3.0	18.7
	8	12.6	3.5	17.3
	9	12.0	4.0	17.1
	10	11.5	4.4	16.6
	11	13.0	3.3	17.5
	12	11.3	5.4	12.8
	13	11.6	4.5	10.9
	14	12.4	3.5	17.2
	15	12.9	3.2	17.6
	16	12.1	4.1	17.2
	17	11.0	5.6	12.7
比較例	18	13.5	2.5	14.8
	19	12.4	3.8	16.5
	20	9.3	1.4	5.2
	21	4.2	0.9	3.2

[0034]

[Table 3]

		熱処理温度 ℃
実施例	1	580～650
	2	600～680
	3	610～700
	4	620～720
	5	615～690
	6	630～740
	7	590～670
	8	610～740
	9	610～700
	10	620～710
	11	590～660
	12	600～690
	13	630～740
	14	620～720
	15	580～670
	16	600～690
	17	630～740
比較例	18	600～650
	19	640～700
	20	-
	21	-

[0035]
[Table 4]

		磁粉特性		
		Br (kG)	iHc (kOe)	(BH)max (MGOe)
実施例	6	7.0	6.9	7.1
	7	8.5	2.9	10.8
	8	7.7	3.5	9.5
	13	7.3	4.5	8.9

[0036]
[Effect of the Invention] This invention is a thing aiming at relaxation of the manufacture conditions in the manufacture approach of the Nd-Fe-B system fine crystal permanent magnet of low rare earth concentration that a soft magnetism phase and a hard magnetism phase are intermingled. The alloy molten metal of the specific presentation in which there are few contents of rare earth elements as less than [6at%], and they contain B of 15at%-30at By facing carrying out quenching alloying with the melt quenching method using a cooling roller, and quenching in the inert gas ambient atmosphere of 31kPa-101kPa The liquid quenching conditions which needed to make amorphous 90% or more of parenchyma are eased conventionally. The magnet alloy which the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in a Fe3B mold compound list lives together, and has the

magnetic properties of iHc>=2kOe and Br>=8kG after heat treatment also on liquid quenching conditions with the crystalline structure of a quenching alloy able to occupy 50% or more is obtained easily.

[0037] Namely, while the deposit of alpha-Fe of 100nm or more of crystal grain parameters which carry out the cause of the degradation of magnetic properties is controlled also on the liquid quenching conditions that the crystalline structure of a quenching alloy occupies 50% or more Then, in case it heat-treats in a 550 degrees C - 750 degrees C temperature region, the compound phase which has alpha-Fe and the Nd2Fe14B mold crystal structure in the Fe3B mold compound list of 10nm - 50nm of diameters of average crystal grain lives together. When the heat-treatment-temperature range which can obtain the fine crystal permanent magnet alloy which obtains the magnet alloy which has the magnetic properties of iHc>=2kOe and Br>=8kG is expanded The manufacture conditions of a fine crystal permanent magnet can ease, it is cheap, and conventionally, on industrial production, stable industrial production cannot be made possible and the fine crystal permanent magnet with the price performance which is equal to a hard ferrite magnet which was not able to be produced cheaply and in large quantities can be offered [it is cheap and].

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which shows the dependency of the coercive force over the heat treatment temperature of the quenching alloy in an example and the example of a comparison.

[Translation done.]

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(54)【発明の名称】　微細結晶永久磁石合金及び永久磁石粉末の製造方法

(57)【要約】

【課題】　希土類濃度が６ａｔ％以下で軟磁性のFe_3B相と硬磁性である$Nd_2Fe_{14}B$相が同一組織内に混在する微細金属組織を有する準安定構造の永久磁石材料において、製造条件を緩和して安価で安定した工業生産を可能にする。

【解決手段】　合金溶湯を３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、冷却ロールにより液体急冷することにより、従来、実質９０％以上まで非晶質化する必要があった液体急冷条件が緩和され、急冷合金の結晶組織が５０％以上を占める液体急冷条件でも、磁気特性の劣化を誘因する結晶粒径数１００ｎｍ以上のα－Ｆｅの析出が抑制されると共に、５５０℃～７５０℃の温度域にて熱処理を施す際、平均結晶粒径１０ｎｍ～５０ｎｍのFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存し、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金を得られる熱処理温度範囲が拡大して、微細結晶永久磁石を安価に量産できる。

【特許請求の範囲】

【請求項１】　組成式を$Fe_{100-x-y}B_xR_y$　（但しRはＰｒ、Ｎｄ、ＤｙまたはＴｂの１種または２種以上）と表し、組成範囲を限定する記号ｘ、ｙが下記値を満足する溶湯を、３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、回転する冷却ロール上に連続的に鋳込み、平均結晶粒径１０ｎｍ以下のFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存する結晶組織が５０％以上を占め、残部が非晶質からなる微細結晶合金を作製し、その後、５５０℃～７５０℃の温度域にて熱処理を施すことで、平均結晶粒径１０ｎｍ～５０ｎｍの微細結晶合金となし、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金の製造方法。

１５≦ｘ≦３０ａｔ％

１≦ｙ＜６ａｔ％

【請求項２】　組成式を$(Fe_{1-m}Co_m)_{100-x-y}B_xR_y$　（但しRはＰｒ、Ｎｄ、ＤｙまたはＴｂの１種または２種以上）と表し、組成範囲を限定する記号ｘ、ｙ、ｍが下記値を満足する溶湯を、３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、回転する冷却ロール上に連続的に鋳込み、平均結晶粒径１０ｎｍ以下のFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存する結晶組織が５０％以上を占め、残部が非晶質からなる微細結晶合金を作製し、その後、５５０℃～７５０℃の温度域にて熱処理を施すことで、平均結晶粒径１０ｎｍ～５０ｎｍの微細結晶合金となし、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金の製造方法。

１５≦ｘ≦３０ａｔ％

１≦ｙ＜６ａｔ％

０．００１≦ｍ≦０．５

【請求項３】　組成式を$Fe_{100-x-y-z}B_xR_yM_z$　（但しRはＰｒ、Ｎｄ、ＤｙまたはＴｂの１種または２種以上、MはＡｌ、Ｓｉ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｎｉ、Ｃｕ、Ｇａ、Ｚｒ、Ｎｂ、Ｍｏ、Ａｇ、Ｐｔ、Ａｕ、Ｐｂの１種または２種以上）と表し、組成範囲を限定する記号ｘ、ｙ、ｚが下記値を満足する溶湯を、３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、回転する冷却ロール上に連続的に鋳込み、平均結晶粒径１０ｎｍ以下のFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存する結晶組織が５０％以上を占め、残部が非晶質からなる微細結晶合金を作製し、その後、５５０℃～７５０℃の温度域にて熱処理を施すことで、平均結晶粒径１０ｎｍ～５０ｎｍの微細結晶合金となし、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金の製造方法。

１５≦ｘ≦３０ａｔ％

１≦ｙ＜６ａｔ％

０．０１≦ｚ≦７ａｔ％

【請求項４】　組成式を$(Fe_{1-m}Co_m)_{100-x-y-z}B_xR_yM_z$　（但しRはＰｒ、Ｎｄ、ＤｙまたはＴｂの１種または２種以上、MはＡｌ、Ｓｉ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｎｉ、Ｃｕ、Ｇａ、Ｚｒ、Ｎｂ、Ｍｏ、Ａｇ、Ｐｔ、Ａｕ、Ｐｂの１種または２種以上）と表し、組成範囲を限定する記号ｘ、ｙ、ｚ、ｍが下記値を満足する溶湯を、３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、回転する冷却ロール上に連続的に鋳込み、平均結晶粒径１０ｎｍ以下のFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存する結晶組織が５０％以上を占め、残部が非晶質からなる微細結晶合金を作製し、その後、５５０℃～７５０℃の温度域にて熱処理を施すことで、平均結晶粒径１０ｎｍ～５０ｎｍの微細結晶合金となし、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金の製造方法。

１５≦ｘ≦３０ａｔ％

１≦ｙ＜６ａｔ％

０．０１≦ｚ≦７ａｔ％

０．００１≦ｍ≦０．５

【請求項５】　請求項１、請求項２、請求項３または請求項４において、得られた微細結晶永久磁石合金を平均粉末粒径３μｍ～５００μｍに粉砕して、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧７ｋＧの磁気特性を有する磁石粉末を得る微細結晶組織を有する等方性永久磁石粉末の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】この発明は、各種小型モーター、アクチュエーター、磁気センサー用磁気回路などに最適な永久磁石合金および永久磁石粉末の製造方法に係り、６ａｔ％以下の希土類元素と１５ａｔ％～３０ａｔ％のホウ素を含む特定組成の溶湯を、特定の減圧不活性ガス雰囲気中、回転する冷却ロール上に特定組成の合金溶湯を連続的に鋳込むことによって、平均結晶粒径１０ｎｍ以下のFe_3B型化合物並びにα‐Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存する結晶組織が５０％以上を占め、残部が非晶質からなる微細結晶合金を作製し、その後、５５０℃～７５０℃の温度域にて熱処理を施すことで、平均結晶粒径を１０ｎｍ～５０ｎｍまで粒成長させることにより、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する永久磁石合金、あるいは永久磁石合金を粉砕することによって、ボンド磁石用磁石粉末として実用に耐えるｉＨｃ≧２ｋＯｅ、Ｂｒ≧７ｋＧの磁気特性を有する永久磁石粉末を得ることが可能な微細結晶永久磁石合金及び永久磁石粉末の製造方法に関する。

【０００２】

【従来の技術】現在、家電用機器、ＯＡ機器、電装品等において、より一層の高性能化と小型軽量化が要求され

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ており、永久磁石を用いた磁気回路全体として、性能対重量比を最大にするための設計が検討されており、特に現在の生産台数の大半を占めるブラシ付き直流モーターの構造では永久磁石として残留磁束密度Ｂｒが５ｋＧ～７ｋＧ程度のものが最適とされているが、従来のハードフェライト磁石では得ることができない。

【０００３】例えば、$Nd_2Fe_{14}B$を主相とする、Ｎｄ－Ｆｅ－Ｂ焼結磁石やＮｄ－Ｆｅ－Ｂボンド磁石ではかかる磁気特性を満足するが、金属の分離精製や還元反応に多大の工程並びに大規模な設備を要するＮｄを１０ａｔ％～１５ａｔ％含有しているため、ハードフェライト磁石に比較して著しく高価となり、性能対価格比の点でハードフェライト磁石からの代替は一部の機種でしか進んでおらず、現在のところ、５ｋＧ以上のＢｒを有し、安価な永久磁石材料は見出されていない。

【０００４】

【発明が解決しようとする課題】一方、Ｎｄ－Ｆｅ－Ｂ系磁石において、近年、$Nd_4Fe_{77}B_{19}$（ａｔ％）近傍組成でFe_3B型化合物を主相する磁石材料が提案（R．Ｃｏｅｈｏｏｒｎ等、Ｊ．ｄｅ　Ｐｈｙｓ，　Ｃ８，　１９８８，　６６９～６７０頁）され、その技術内容は米国特許４，９３５，０７４等に開示されている。

【０００５】また、Ｋｏｏｎはそれよりも以前に、Ｌａを必須元素として含むＬａ－Ｒ－Ｂ－Ｆｅアモルファス合金に結晶化熱処理を施すことによる、微細結晶からなる永久磁石の製造方法を米国特許４，４０２，７７０にて提案している。

【０００６】最近ではＲｉｃｈｔｅｒらによってＥＰ特許５５８６９１Ｂ１に開示されているように、Ｎｄを３．８ａｔ％～３．９ａｔ％含有するＮｄ－Ｆｅ－Ｂ－Ｖ－Ｓｉ合金溶湯を回転するＣｕロール上に噴射して得られたアモルファスフレークを７００℃で熱処理することにより、硬磁気特性を有す薄片が得られることを報告している。

【０００７】これらの永久磁石材料は、厚み２０μｍ～６０μｍのアモルファスフレークに結晶化熱処理を施すことによって得られる、軟磁性であるFe_3B相と硬磁性である$R_2Fe_{14}B$相が混在する結晶集合組織を有する準安定構造の永久磁石材料である。

【０００８】かかる永久磁石材料は、１０ｋＧ程度のＢｒと２ｋＯｅ～３ｋＯｅのｉＨｃを有し、高価なＮｄの含有濃度が４ａｔ％程度と低いため、配合原料価格は$Nd_2Fe_{14}B$を主相とするＮｄ－Ｆｅ－Ｂ磁石より安価ではあるが、配合原料を実質９０％以上非晶質合金化する必要があるため液体急冷条件が限定され、また、同時に硬磁性材料になり得るための熱処理条件が狭く限定され、工業生産上実用的でなく、ハードフェライト磁石の代替として安価に提供できない。

【０００９】他方、米国特許５０８，２６６等の超急冷

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Ｎｄ－Ｆｅ－Ｂ系磁石材料では、合金溶湯をロール周速度２０ｍ／ｓ程度で急冷することにより直接、硬磁気特性を有する結晶質からなる組織を得られるが、合金に含有される高価なＮｄ含有量が１３ａｔ％程度と高いため、ハードフェライト磁石の代替として安価に提供できない。

【００１０】この発明は、希土類濃度が６ａｔ％以下と低いことを特徴とする軟磁性のFe_3B相と硬磁性の$Nd_2Fe_{14}B$相が混在する結晶集合組織を有する準安定構造の永久磁石材料において、その製造条件、特に熱処理条件を緩和して安定した工業生産を可能にすることを目的とし、特に８ｋＧ以上の残留磁束密度Ｂｒを有し、ハードフェライト磁石に匹敵する性能対価格比を有する微細結晶永久磁石合金を量産可能にする微細結晶永久磁石合金の製造方法の提供を目的としている。

【００１１】

【課題を解決するための手段】発明者らは、軟磁性相と硬磁性相が混在する低希土類濃度のＮｄ－Ｆｅ－Ｂ系微細結晶永久磁石の製造方法を種々検討した結果、希土類元素の含有量が６ａｔ％以下と少なく、１５ａｔ％～３０ａｔ％のＢを含有する特定組成の合金溶湯を、冷却ロールを用いた液体急冷法により急冷合金化するに際し、３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、急冷することにより、従来、実質９０％以上に非晶質化する必要があった液体急冷条件が緩和され、急冷合金の結晶組織が５０％以上を占める液体急冷条件でも、磁気特性の劣化を誘因する結晶粒径数１００ｎｍ以上のα－Ｆｅの析出が抑制されると共に、その後、５５０℃～７５０℃の温度域にて熱処理を施す際、平均結晶粒径１０ｎｍ～５０ｎｍのFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存し、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金を得られる熱処理温度範囲が拡大することを知見し、この発明を完成した。

【００１２】すなわち、この発明は、組成式を$Fe_{100-x-y}B_xR_y$、$(Fe_{1-m}Co_m)_{100-x-y}B_xR_y$、$Fe_{100-x-y-z}B_xR_yM_z$、$(Fe_{1-m}Co_m)_{100-x-y-z}B_xR_yM_z$

（但しＲはＰｒ、Ｎｄ、ＤｙまたはＴｂの１種または２種以上、ＭはＡｌ、Ｓｉ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｎｉ、Ｃｕ、Ｇａ、Ｚｒ、Ｎｂ、Ｍｏ、Ａｇ、Ｐｔ、Ａｕ、Ｐｂの１種または２種以上）のいずれかで表し、組成範囲を限定する記号ｘ、ｙ、ｚ、ｍが下記値を満足する溶湯を、３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、回転する冷却ロール上に連続的に鋳込み、平均結晶粒径１０ｎｍ以下のFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存する結晶組織が５０％以上を占め、残部が非晶質からなる微細結晶合金を作製し、その後、５５０℃～７５０℃の温度域にて熱処理を施すことで、平均結晶粒径１０

ｎｍ～５０ｎｍの微細結晶合金となし、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金の製造方法を提案するものである。
１５≦ｘ≦３０ａｔ％
１≦ｙ＜６ａｔ％
０．０１≦ｚ≦７ａｔ％
０．００１≦ｍ≦０．５

【００１３】さらに、この発明は、前述の製造方法にて得られる微細結晶永久磁石合金を平均粉末粒径３μｍ～５００μｍに粉砕して、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧７ｋＧの磁気特性を有する磁石粉末を得る微細結晶組織を有する等方性永久磁石粉末の製造方法を併せて提案する。

【００１４】

【発明の実施の形態】

組成の限定理由

希土類元素Ｒは、Ｐｒ、Ｎｄ、ＤｙまたはＴｂの１種または２種以上を特定量含有のときのみ、高い磁気特性が得られ、他の希土類、例えばＣｅ、ＬａではｉＨｃが２ｋＯｅ以上の特性が得られず、また、Ｔｂ、およびＤｙを除くＳｍ以降の中希土類元素、重希土類元素は磁気特性の劣化を招来するため好ましくない。Ｒは、１ａｔ％未満では２ｋＯｅ以上のｉＨｃが得られず、また６ａｔ％を越えると８ｋＧ以上のＢｒが得られないため、１ａｔ％以上６ａｔ％未満の範囲とする。好ましくは、２ａｔ％～５．５ａｔ％が良い。

【００１５】Ｂは、１５ａｔ％未満では液体急冷後の金属組織において、α－Ｆｅの析出が著しく、保磁力の発現に必須である$Nd_2Fe_{14}B$型結晶構造を有する化合物の析出が阻害されるため、１ｋＯｅ未満のｉＨｃしか得られない、また３０ａｔ％を越えると減磁曲線の角形性が著しく低下し、８ｋＧ以上のＢｒが得られないため、１５ａｔ％～３０ａｔ％の範囲とする。好ましくは、１５ａｔ％～２０ａｔ％が良い。

【００１６】Ｆｅは、上述の元素の含有残余を占め、Ｆｅの一部をＣｏで置換することにより金属組織が微細化され、減磁曲線の角形性が改善、及び最大エネルギー積（ＢＨ）ｍａｘの向上、並びに耐熱性の向上が得られるが、Ｆｅに対する置換量が０．１％未満ではかかる効果が得られず、また、５０％を越えると８ｋＧ以上のＢｒが得られないため、ＣｏのＦｅに対する置換量は０．１％～５０％の範囲とする。好ましくは、０．５％～１０％が良い。

【００１７】添加元素ＭのＡｌ、Ｓｉ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｎｉ、Ｃｕ、Ｇａ、Ｚｒ、Ｎｂ、Ｍｏ、Ａｇ、Ｐｔ、Ａｕ、Ｐｂは、微細結晶永久磁石の微細組織化に寄与し、保磁力を改善すると共に、減磁曲線の角形性を改善し、Ｂｒおよび（ＢＨ）ｍａｘを増大する効果が得られるが、０．０１ａｔ％未満ではかかる効果が得られず、７ａｔ％以上ではＢｒ≧８ｋＧの磁気特性を得られないため、０．０１ａｔ％～７ａｔ％の範囲とする。好ましくは、０．０５ａｔ％～５ａｔ％である。

【００１８】製造条件の限定理由

この発明において、上述の特定組成の合金溶湯を３１ｋＰａ～１０１ｋＰａの範囲の不活性ガス雰囲気中にて、回転する冷却ロール上に連続的に鋳込み、平均結晶粒径１０ｎｍ以下のFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存する結晶組織が５０％以上を占め、残部が非晶質からなる微細結晶合金を作製し、その後、５５０℃～７５０℃の温度域にて熱処理を施すことで、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得るに必要な平均結晶粒径１０ｎｍ～５０ｎｍの微細結晶組織となすことが最も重要である。

【００１９】すなわち、合金溶湯の連続鋳造の際、鋳造雰囲気が１０１ｋＰａを越える場合は、ロールと溶湯間のガス巻き込み、およびロール周辺の風による溶湯流の乱れなどにより、冷却条件が安定しない結晶粒径数１００ｎｍの粗大なα－Ｆｅを含む急冷合金組織となり、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性が得られず、３１ｋＰａ未満の場合は、合金組成に依存して変化するアモルファス形成能が増大して過急冷となりやすく、熱処理後の磁気特性が安定しないことから、溶湯急冷雰囲気を３１ｋＰａ～１０１ｋＰａとする。好ましくは、３１ｋＰａ～８０ｋＰａが良い。雰囲気ガスは、合金溶湯の酸化防止のため、不活性ガス雰囲気とする。好ましくは、N_2、Ａｒ雰囲気中が良い。

【００２０】前述の急冷合金は、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する永久磁石合金を得るのに必要な平均結晶粒径１０ｎｍ～５０ｎｍの微細結晶からなる金属組織になるよう、結晶粒成長を目的とした熱処理を行う必要があるが、熱処理温度が５５０℃未満では粒成長を起こさないため、１０ｎｍ以上の平均結晶粒径が得られない、また７５０℃を越えると粒成長が著しくｉＨｃ、Ｂｒおよび減磁曲線の角形性が劣化し、上述の磁気特性が得られないため、熱処理温度は５５０℃～７５０℃に限定する。

【００２１】熱処理において、雰囲気は酸化を防ぐためＡｒガス、N_2ガスなどの不活性ガス雰囲気中もしくは１．３３Ｐａ以下の真空中が好ましい。磁気特性は熱処理時間には依存しないが、６時間を越えるような場合、若干時間の経過とともにＢｒが低下する傾向があるため、好ましくは６時間未満が良い。

【００２２】合金溶湯の液体急冷連続鋳造処理に用いる冷却ロールの材質は、熱伝導度の点からアルミニウム合金、純銅および銅合金、鉄、真鍮、タングステン、青銅を採用できるが、機械的強度および経済性の点から、ＣｕもしくはＦｅ（但しＣｕ、Ｆｅを含む合金でもよい）が好ましく、上記以外の材質では熱伝導が悪いため、充分合金溶湯を冷却できず、数１００ｎｍの粗大なα－ＦｅおよびFe_2Bが析出するため、ｉＨｃ≧２ｋＯｅ、

Ｂｒ≧８ｋＧの磁気特性を得られず好ましくない。

【００２３】例えば、冷却ロールに中心線粗さＲａ≦０．８μｍ、最大高さＲｍａｘ≦３．２μｍ、１０点の平均粗さＲｚ≦３．２μｍの表面粗度を有するＣｕ製ロールを採用した場合、ロール周速度が１５ｍ／ｓを越えると急冷合金中に含まれる結晶組織が５０％以下となり、非晶質相が増加するため好ましくなく、また、ロール周速度が４ｍ／ｓ以下の場合、急冷合金の金属組織が不均一となり、熱処理後の磁気特性が安定せず好ましくないため、ロール周速度は、４ｍ／ｓ～１５ｍ／ｓが良い。

【００２４】また、この発明による微細結晶永久磁石合金を３μｍ～５００μｍの粒度になるよう粉砕することにより、ｉＨｃ≧４ｋＯｅ、Ｂｒ≧７ｋＧを有する等方性永久磁石磁粉末を得ることができる。粉末粒径が３μｍ未満では磁気特性、特にＢｒが低下し好ましくなく、また、５００μｍを越えると成形が困難なため、粉砕後の磁粉粒度を３μｍ～５００μｍに限定する。圧縮成形ボンド磁石用磁粉として利用する場合は１０μｍ～３００μｍが好ましく、射出成形ボンド磁石用磁粉としては５０μｍ以下が好ましい。

【００２５】この発明による微細結晶永久磁石合金の結晶相は、軟磁性を有するFe_3B型化合物ならびにα－Ｆｅと、$Nd_2Fe_{14}B$型結晶構造を有する硬磁性化合物相とが同一組織中に共存し、各構成相の平均結晶粒径が１０ｎｍ～５０ｎｍの範囲の微細結晶集合体からなることを特徴としている。微細結晶永久磁石合金を構成する平均結晶粒径が５０ｎｍを越えると、Ｂｒおよび減磁曲線の角形性が劣化し、Ｂｒ≧８ｋＧの磁気特性を得ることができない。また、平均結晶粒径は細かいほど好ましいが、１０ｎｍ未満ではｉＨｃの低下を引き起こすため、下限を１０ｎｍとする。

【００２６】

【実施例】

実施例１

表１のＮｏ．１～１７の組成となるように、純度９９．５％以上のＦｅ、Ｃｏ、Ａｌ、Ｓｉ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｎｉ、Ｃｕ、Ｇａ、Ｚｒ、Ｎｂ、Ｍｏ、Ａｇ、Ｐｔ、Ａｕ、Ｐｂ、Ｂ、Ｎｄ、Ｐｒ、Ｄｙ、Ｔｂの金属を用い、総量が３０ｇとなるように秤量し、底部に直径０．８ｍｍのオリフィスを有する石英るつぼ内に投入し、表１の急冷雰囲気圧に保持したＡｒ雰囲気中で高周

波加熱により溶解し、溶解温度を１３００℃にした後、湯面をＡｒガスにより加圧して室温にて、表１に示す急冷雰囲気およびロール周速度にて回転するＣｕ製冷却ロールの外周面に０．７ｍｍの高さから溶湯を連続して鋳込み幅２ｍｍ～３ｍｍ、厚み１００μｍ～３００μｍの連続した薄板状の急冷合金を作製した。

【００２７】この急冷合金をＡｒガス中で、表１に示す熱処理温度で１０分間保持し、その後室温まで冷却して合金を取り出し、幅２～３ｍｍ、厚み５０μｍ～２００μｍ、長さ３～５ｍｍの試料を作製し、ＶＳＭにて測定した。表２に磁石特性を示す。Ｎｏ．３～Ｎｏ．１７においてＣｏ、Ａｌ、Ｓｉ、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｎｉ、Ｃｕ、Ｇａ、Ｚｒ、Ｎｂ、Ｍｏ、Ａｇ、Ｐｔ、Ａｕ、Ｐｂは各構成相のＦｅの一部を置換する。

【００２８】図１の実施例Ｎｏ．８における熱処理温度に対する保磁力依存性が示す如く、この発明により得られる急冷合金の保磁力は、熱処理温度に依存する。表３に実施例Ｎｏ．１～Ｎｏ．１７の急冷合金において、２ｋＯｅ以上のｉＨｃが得られる熱処理温度域を示す。

【００２９】実施例２

表１のＮｏ．６、Ｎｏ．７、Ｎｏ．８、Ｎｏ．１３の急冷合金については、粉砕機を用いて粉砕粒度２５μｍ～３００μｍ、平均粉末粒径１５０μｍになるよう粉砕し、等方性永久磁石粉末を作製した。表４にＶＳＭにて測定した磁石粉末の磁気特性を示す。

【００３０】比較例１

表１のＮｏ．１８～Ｎｏ．２１の組成となるように純度９９．５％のＦｅ、Ｂ、Ｒ、Ｓｉを用いて表１に示す急冷条件で急冷合金を作製した。得られた急冷合金に熱処理を施し、冷却後に実施例１と同一条件で試料を作製してＶＳＭを用いて磁気特性を評価した。評価結果を表２に示す。

【００３１】比較例Ｎｏ．１９の磁気特性は、図１の熱処理温度に対する保磁力依存性が示す如く、熱処理温度に依存するが、保磁力の発現する熱処理温度域は、急冷雰囲気圧６０ｋＰａにて得られた実施例Ｎｏ．８に比べ狭い。表３に比較例Ｎｏ．１８～Ｎｏ．２１の急冷合金において、２ｋＯｅ以上のｉＨｃが得られる熱処理温度域を示す。

【００３２】

【表１】

		組成(at%)				ロール周速度	急冷雰囲気圧	熱処理温度
		Fe	B	R	M	m/秒	kPa	℃
実施例	1	79.5	18.5	Nd2	-	10	50	590
	2	78.5	18.5	Nd3	-	15	80	620
	3	75+Co3	17.5	Nd3.5+Pr1	-	7	50	640
	4	70+Co2	20	Nd5	V3	7	40	660
	5	77+Co3	15.5	Nd4	Zr0.5	4	40	640
	6	66+Co5	18.5	Nd5.5	Cr5	12	31	700
	7	78	17	Nd3	Al2	8	70	600
	8	76.5	18.5	Nd4	Si1	5	60	680
	9	69	18.5	Nd3.5+Dy1	Mn1	10	80	640
	10	76	20	Nd5	Ni1.5	10	50	660
	11	75	20	Nd2.5+Pr1	Cu1.5	10	50	610
	12	77	18.5	Nd2+Dy2	Nb0.5	10	50	620
	13	75.5	18.5	Nd2+Pr3	Ga1	8	40	660
	14	76.5	18.5	Nd4	Ag1	8	40	660
	15	78	18	Nd3.5	Pt0.5	8	40	600
	16	76.5	18.5	Nd4.5	Au0.5	6	55	640
	17	75.5	18.5	Nd4.5+Tb0.5	Pb1	9	35	680
比較例	18	78.5	18.5	Nd3	-	30	110	615
	19	76.5	18.5	Nd4	Si1	20	110	660
	20	75.5	18.5	Nd3	-	10	110	620
	21	76.5	18.5	Nd4	Si1	5	110	670

【0033】
【表2】

		磁石特性		
		Br (kG)	iHc (kOe)	(BH)max (MGOe)
本発明	1	15.0	2.0	13.5
	2	13.7	2.7	15.0
	3	11.4	4.2	14.7
	4	10.0	6.0	12.2
	5	12.3	4.5	15.5
	6	10.1	6.9	12.9
	7	13.4	3.0	18.7
	8	12.6	3.5	17.3
	9	12.0	4.0	17.1
	10	11.5	4.4	16.6
	11	13.0	3.3	17.5
	12	11.3	5.4	12.8
	13	11.6	4.5	10.9
	14	12.4	3.5	17.2
	15	12.9	3.2	17.6
	16	12.1	4.1	17.2
	17	11.0	5.6	12.7
比較例	18	13.5	2.5	14.8
	19	12.4	3.8	16.5
	20	9.3	1.4	5.2
	21	4.2	0.9	3.2

【００３４】

【表３】

		熱処理温度 ℃
実施例	1	580～650
	2	600～680
	3	610～700
	4	620～720
	5	615～690
	6	630～740
	7	590～670
	8	610～740
	9	610～700
	10	620～710
	11	590～660
	12	600～690
	13	630～740
	14	620～720
	15	580～670
	16	600～690
	17	630～740
比較例	18	600～650
	19	640～700
	20	-
	21	-

【００３５】

【表４】

		磁粉特性		
		Br (kG)	iHc (kOe)	(BH)max (MGOe)
実施例	6	7.0	6.9	7.1
	7	8.5	2.9	10.8
	8	7.7	3.5	9.5
	13	7.3	4.5	8.9

【００３６】

【発明の効果】この発明は、軟磁性相と硬磁性相が混在する低希土類濃度のＮｄ－Ｆｅ－Ｂ系微細結晶永久磁石の製造方法における製造条件の緩和を図ったもので、希土類元素の含有量が６ａｔ％以下と少なく、１５ａｔ％～３０ａｔのＢを含有する特定組成の合金溶湯を、冷却ロールを用いた液体急冷法により急冷合金化するに際し、３１ｋＰａ～１０１ｋＰａの不活性ガス雰囲気中にて、急冷することにより、従来、実質９０％以上を非晶質化する必要があった液体急冷条件が緩和され、急冷合金の結晶組織が５０％以上を占めることが可能な液体急冷条件でも、熱処理後にFe_3B型化合物並びにα－Ｆｅと$Nd_2Fe_{14}B$型結晶構造を有する化合物相が共存

してｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金が容易に得られる。

【００３７】すなわち、急冷合金の結晶組織が５０％以上を占める液体急冷条件でも、磁気特性の劣化を誘因する結晶粒径数１００ｎｍ以上のα－Ｆｅの析出が抑制されると共に、その後、５５０℃～７５０℃の温度域にて熱処理を施す際、平均結晶粒径１０ｎｍ～５０ｎｍのＦe_3Ｂ型化合物並びにα－ＦｅとＮd_2Ｆe_{14}Ｂ型結晶構造を有する化合物相が共存し、ｉＨｃ≧２ｋＯｅ、Ｂｒ≧８ｋＧの磁気特性を有する磁石合金を得る微細結晶永久磁石合金を得られる熱処理温度範囲が拡大することによって、微細結晶永久磁石の製造条件の緩和して安価で安定した工業生産を可能にできるもので、従来、工業生産上、安価で大量に生産することができなかった、ハードフェライト磁石に匹敵する性能対価格比をもつ微細結晶永久磁石を安価で提供できる。

【図面の簡単な説明】

【図１】実施例及び比較例における急冷合金の熱処理温度に対する保磁力の依存性を示すグラフである。

【図１】